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IS 13673 (Part 2) : 1993

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विद्युत रासायनिक विश्लेषक कार्यकारिता की अभिव्यक्ति

भाग 2 पी एच मान

Indian Standard

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 2 *p*H VALUE

UDC 621·35·035 : 543·2·57·1·08

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

June 1993 Price Group 4

Electronic Measuring Equipment Sectional Committee, LTD 21

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Electronic Measuring Equipment Sectional Committee had been approved by the Electronics and Telecommunication Division Council.

This standard is intended to specify the terminology, definitions, requirements for statements by manufacturers and performance tests for analyzers, sensor units and electronic units used for the determination of electrolytic conductinity of aqueous solutions.

While preparing this standard (Part 3), assistance has been derived from IEC Pub 746-3 (1985), 'Expression of performance of electrochemical analyzers — Part 3 : Electrolytic conductinity', issueed by the International Electrotechnical Commission (IEC).

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it should be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

AMENDMENT NO. 1 SEPTEMBER 1998
TO
IS 13673 (PART 2) : 1993 EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 2 *p*H VALUE

(*Second cover page, Foreword, para* 3, *lines* 1 *and* 2) — Substitute 'IEC Pub 746-2 (1982) Expression of performance of electrochemical analyzers — Part 2 : *p*H value' *for* 'IEC Pub 746-3 (1985) Expression of performance of electrochemical analyzers — Part 3 : Electrolytic conductivity'.

(LTD 21)

Reprography Unit, BIS, New Delhi, India

Indian Standard

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 2 *p*H VALUE

1 SCOPE

1.1 This standard lays down performance tests and requirements for statements by manufacturers of analyzers, sensor units and electronic units used for the determination of *p*H values of aqueous solutions using glass-electrodes.

1.2 It also contains specifications for simulators used for testing *p*H electronic units.

2 REFERENCES

2.1 The Indian Standard listed below is a necessary adjunct to this standard.

IS No.	*Title*
13673 (Part 1) :1992	Expression of performance of Electrochemical analyzers : Part 1 General

3 DEFINITIONS AND SYMBOLS

See 3 of IS 13673 (Part 1) :1992 plus the following.

3.1 Symbols

aH^+ = hydrogen ion activity

pH = *p*H of the solution measured at temperature *t*

$pH\ (S_1)$ = *p*H of the first reference buffer solution, at temperature *t*

$pH\ (S_2)$ = *p*H of the second reference buffer

pH_i = *p*H at isopotential point

E = electromotive force in the measured sample at temperature *t*

$E(S_1)$ = electromotive force in the first reference buffer solution, at temperature *t*

$E\ (S_2)$ = electromotive force in the second reference buffer solution, at temperature *t*

E_i = electromotive force at the isopotential point

F = the Faraday constant

R = the molar gas constant

t = temperature in degree Celsius

T = The thermodynamic temperature in degree Kelvin of sample, buffer solutions and sensors ($T=t + 273.15$)

3.2 *p*H Value

A measure of the conventional hydrogen ion activity aH^+ in an aqueous solution given by the expression:

$$pH = -\log aH^+$$

Although this expression can be used to give an interpretation to *p*H values under certain limiting conditions, aH^+ cannot be rigorously obtained from electromotive force measurements, and an operational definition is adopted in terms of *p*H values assigned to certain reference buffers. The measurement is performed by determining the e.m.f. *E* between a pair of electrodes immersed in the sample to be measured, according to the cell scheme:

Reference electrode | Sample | Glass electrode *E*

and a measurement with the same electrode pair at the same temperature in a reference buffer solution of *p*H (S_1) according to:

Reference electrode| Reference (S_1)| Glass electrode E (S_1)

The e.m.f.'s *E*, *E* (S_1), etc are defined as the difference of the potential of the right-hand (glass electrode) minus the potential of the left-hand (reference electrode).

The *p*H of the sample is then given by:

$$pH = pH\ (S_1) - \frac{[E\ E\ (S_1)]}{k} \qquad ...(1)$$

where $k = 2.302\,6\ RT/F$.

Numerical values for *k*, which is known as the theoretical slope factor, at temperatures from 0 to 95°C, are given in Annex A.

3.3 Percentage of Theoretical Slope (PTS)

Under some conditions, the performance of the electrode pair may fall below the theoretical expectation, that is, below the value of *k* at the appropriate temperature. Such deviation is expressed as a percentage of the theoretical slope (PTS) and may be determined by replacing the sample by a second reference buffer of *p*H value *p*H (S_2) which yields an indicated e.m.f. of S (S_2), then:

$$PTS = \frac{100\ [E\ (S_2) - E\ (S_1)]}{k\ [pH\ (S_1) - p\ H\ (S)]} \qquad ...(2)$$

NOTE — For the best accuracy, the difference in *p*H value between the two reference buffer solutions should be as large as possible. However, neither solutions A nor I given in Annex B should be used.

Equations (1) and (2) can be combined by substituting the practical slope *k*' for factor *k* in equation (1), where

$$k' = \frac{k\ (PTS)}{100}$$

$$pH = pH\ (S_1) = \frac{[E - E\ (S_1)]\ [\,pH\ (S_1) - pH\ (S_2)]}{[E\ (S_1) - E\ (S_2)]}$$

and the two reference buffers are usually chosen to bracket the *p*H of the sample.

3.4 Zero Point (*p*H)

The *p*H value at which the *p*H measuring cell (sensor unit) reads O V at a given temperature. If not otherwise specified temperature is understood to be 25°C.

3.5 Isopotential Point of the Sensor Unit

The point of intersection on an e.m.f. versus *p*H plot of *p*H calibration curves taken at different temperatures. The isopotential point is dependent on the temperature coefficients of both *p*H and reference electrodes. The co-ordinates are pH_i and E_i. Using these co-ordinates, the *p*H value of the sample can be calculated by:

$$pH = pH_i - \frac{[E - E_i]}{k'}$$

3.6 Sodium Error

The error in the e.m.f. caused by sensitivity of the *p*H electrode for sodium ions.

3.7 Reference Buffer Solution

An aqueous solution prepared according to a specific formula, using recognized analytical grade chemicals and water having a conductivity of no more than 2 μS. cm^{-1}.The *p*H value of reference buffer solutions may, because of the variations in the purity of available commercial chemicals, differ by as much as ± 0.01 from accepted values. For higher accuracy, solutions may be prepared with chemicals that have been characterized and certified by a national standards laboratory.

3.8 Input Offset Voltage

A voltage that is applied between the input terminals to obtain zero output voltage.

3.9 Common Mode Input Voltage

A voltage that is applied to both input terminals at the same time.

3.10 Input Common Mode Rejection Ration (CMPR)

The ratio of the input voltage range to the maximum change in input offset voltage over this range.

4 PROCEDURE FOR STATEMENT

See 4 of IS 13673 (Part 1) : 1993

The manufacturer shall provide statements on the sensor unit and the electronic unit as indicated in **4.1** and **4.3**.

NOTES

1 Linearity and warm-up statements are not required for sensor units. For complete analyzers, statements on linearity and warm-up refer only to the electronic units and are validated as in IS. 13673 (Part 1) : 1993

2 Errors and error limits should be stated in *p*H values.

4.1 Additional Statements on Sensor Units and Analyzers

i) Isopotential Point.

ii) Zero Point (*p*H).

4.2 Additional Statements on Electronic Units

i) Rated Input Offset Range (Buffer Adjustment Range).

ii) Rated automatic-temperature-compensated range of use, and type of compensating element. If only manual temperature compensation is provided, this should be stated.

iii) Slope Adjustment Range.

iv) Input Resistance.

v) Input Offset Voltage at Resistance Temperature

vi) Maximum Allowable Common Mode Input Voltage.

vii) Common Mode Rejection Ratio.

4.3 Statements on Electrodes

i) Reference Electrodes.

ii) Resistance (including junction) at 25°C or at a specified temperature.

NOTE — The resistance may be significantly higher at lower temperatures.

iii) Flow rate of the electrolyte at room temperature, at a given hydrostatic pressure.

iv) Rated range of sample temperature.

v) Type of internal reference system, including a statement on the chemical composition and concentration of the electrolyte and operating range of electrodes.

4.3.2 *Glass Electrodes*

i) Nominal resistance at 25°C or at a specified temperature;

NOTE — The resistance may be significantly higher at lower temperatures.

ii) Insulation resistance between the internal conductor to the internal reference electrode and the shield on the plug termination, in ohms, at 25°C or at a specified temperature ;

iii) Sodium error ;

iv) Rated range of sample temperature ;

v) Rated range of sample *p*H value; and

vi) Type of internal reference system.

5 RECOMMENDED STANDARD VALUES AND RANGES OF INFLUENCE QUANTITIES AFFECTING THE PERFORMANCE OF ELECTRONIC UNITS

See 5 of IS 13673 (Part 1) : 1993.

6 VERIFICATION OF VALUES

See 6 of IS 13673 (Part 1) : 1993, plus the following.

6.1 General Aspects

6.1.1 Compliance tests shall be performed with the apparatus ready for use (including accessories) after warm-up time and after adjustments have been made in accordance with the manufacturer's instructions.

6.1.2 Prior to testing, glass electrodes shall be hydrated by placing them in a buffer solution for 15 min or until there has been no detectable output change for at least 2 min (at least 12 h shall be allowed for initial equilibration on new electrodes).

6.1.3 During all measurements with more than one test solution, the following sensor unit treatment shall be followed unless otherwise indicated:

The electrode pair (sensor unit) shall be carefully rinsed with deionized water, hereafter pre-rinsing with the new solution and only then may it be immersed in the beaker filled with fresh solution. The beakers shall be refilled each time in case several series of measurements are specified. In every case, measurements shall be made in permanently stirred solutions.

6.1.4 Reference buffer solutions shall be used for all tests unless otherwise indicated. *See* **3.4** of IS 13673 (Part 1) : 1993 and Annex B and Annex C.

6.2 Simulators for Testing Electronic Unit

The basic function of simulators for testing electronic units used with *p*H sensor units is to supply Nernstian e.m.f., s, representing known *p*H values, through very high series resistors, representative of *p*H sensor units.

The simulator consists of a stepped voltage divider supplied by a stabilized adjustable voltage source and followed by selectable series resistors.

The network should be such that the output voltage steps represent multiples (or sub-multiples in case of expanded scale electronic units) of e.m.f. representing *p*H steps of one for example 59.16 mV when simulated, temperatures is 25°C. The e.m.f. steps representing a change in *p*H value of one should be adjustable from 50 mV to 80 mV in order to simulate various temperatures. The range of output voltage should be at least from – 500 mV to + 500 mV.

The resistance of the voltage divider network should be no higher then 10 *k* while the selectable series resistors should be in the range of 100 M to 20 M.

6.3 Test Procedures for Sensor Units and Analyzers

In the case of special applications where these tests are not appropriate, additional test procedures may be agreed upon between manufacturer and user.

In any case, the electronic unit shall be tested, separately from the sensor unit, with a simulator as specified under **6.2**. An electronic unit which has been tested successfully in this way is referred to as an 'appropriate electronic unit' in **6.3.2.1** and following.

6.3.1 *Operating Error*

See **6.3.6**.

6.3.2 *Repeatability*

6.3.2.1 *Sensor Unit*

Using an appropriate electronic unit, perform the test as indicated in **6.3.2.2**.

6.3.2.2 *Analyzer*

The sensor unit is exposed to test solutions representing as nearly as possible the minimum, the maximum and the median rated values. The steps are repeated *N* times (where $N > 6$) on each test solution in turn, with no rinsing between the readings, at 25°C or room temperature, at intervals of about ten times the instrument's 90 percent time. The standard deviation is calculated for each set of recorded values for each solution. The mean standard deviation is calculated and reported as 'repeatability'.

The temperature of all solutions shall be the same within ± 0.2°C and reported together with the repeatability.

The sensor unit shall be inserted into the solutions as instructed by the manufacturer.

6.3.3 *Stability*

6.3.3.1 *Sensor unit*

Using and appropriate electronic unit, perform the test as indicated in **6.3.3.2**.

6.3.3.2 *Analyzer*

The sensor unit is exposed to a test solution representing as nearly as possible the mid-scale rated *p*H value and the indicated value is recorded.

This is repeated after the time interval chosen from those listed in **6.7.4** of IS 13673 (Part 1) : 1993 and the stability is calculated and reported in terms of *p*H.

The temperature of solution and sensor unit shall be constant within ± 0.2°C and reported together with the stability.

6.3.4 *Output Fluctuation for Analyzer*

For this test, the analyzer output is to be displayed on a strip chart recorder whose response time is at least as short as that of the analyzer.

The sensor unit is exposed to a test solution representing the approximately mid-scale *p*H value, at any constant temperature within the rated range of sample temperature, for a period of 5 min and the maximum peak-to-peak value of the random or regular deviations from the mean output is determined in terms of *p*H.

The test is repeated three times and the average of the readings is reported.

NOTE — For the purposes of this standard, spikes caused by the influence of external electromagnetic fields or by supply mains spikes are considered as due to changes in influence quantities and are therefore ignored in the determination of output fluctuation.

6.3.5 *Delay Time (T_{10}), Rise (Fall) Time (T_r, T_f), 90 percent Time (T_{90})*

These properties are usually a function of the particular application rather than the instrument. Therefore, it is advisable to design the test in line with the application in so far as possible. Two procedures are described in Annex D. Method A is preferred and obligatory if flow cells are involved.

6.3.6 *Operating Period*

The purpose of this procedure is to test the analyzer or sensor unit under worst case conditions thus substituting for complete verification of operating error. However, the test procedure is under consideration. The basic problem is to determine an appropriate test solution since the presence of varying amounts of contaminating substances (grease, proteins, algae etc) in many of the typical waters for which this standard applies has a substantial effect on the operating period. For this reason, the test should be agreed upon between manufacturer and user.

NOTE — The time interval for operating period should be chosen from the same list as used for stability (*see* 6.7.4 of IS 13673 (Part 1) : 1993.

6.3.7 *Effect of Sample Temperature*

6.3.7.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as indicated in **6.3.7.2.**

6.3.7.2 *Analyzer*

The sensor unit is immersed successively in two containers, filled with a reference buffer representing the rated *p*H value differing as much as possible from the isopotential point (*see* Annex B).

The temperature of the solution in the first container is to be the minimum value of the rated operating range and the temperature of the solution in the second container is to be the maximum value of the rated operating range. Adequate immersion depth of the cell shall be maintained in each case.

The two steady-state indicated values are reported alongwith the respective temperatures.

NOTE — In *p*H measurement the sample temperature has several basic effects on the value indicated by an analyzer:

a) By changing the e.m.f. of the galvanic cell with constant hydrogen ion activity as given in the nearest equation.

b) By changing the hydrogen ion activity of the filling buffer solution of the glass electrode.

c) By changing the hydrogen ion activity of the sample.

d) By changing the difference in potential between the internal and external reference electrodes.

It is possible to compensate for effect given at (a) but not for effects given at (b), (c) and (d). It would be theoretically possible to compensate for effect given at (b) if the variation of the isopotential point with temperature were known.

6.3.8 *Isopotential Point*

6.3.8.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as indicated in **6.3.8.2.**

6.3.8.2 *Analyzer*

Select two reference buffer solutions differing by about 5 in *p*H value for example, *B* and *G* of Annex B. Measure the e.m.f. in each of these reference buffer solutions, first at a temperature T_1 ± 0.2°C, about 50°C higher than T_1.

Allow at least 1 h for the electrodes to equilibrate at the higher temperature. Plot e.m.f. versus *p*H, where the value of *p*H at each of the temperatures is obtained from Annex B. Join the points for T_1, and similarly for these at T_2. The isopotential point (pH_i, E_i) is given by the intersection of the two lines.

6.3.9 *Zero Pint (pH)*

6.3.9.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as indicated in **6.3.9.2.**

6.3.9.2 *Analyzer*

The sensor unit is immersed successively in containers, each filled with one of the *B* through *H* reference buffer solutions listed in Annex B. As many of these buffer solutions are used as lie within the rated range of the unit. The temperature of each buffer solution is held at a constant value within ± 0.2°C while in use. The e.m.f. (*E*) is read for each solution after a steady value has been reached. A linear regression analysis is performed for *E* versus the *p*H value for each solution at the appropriate temperature.

The zero point is the calculated *p*H value corresponding to $E = O$.

6.4 Test Procedures for Electronic Units

6.4.1 *Common Mode Rejection Ratio (CMRR)*

The maximum rated common mode input voltage (V_c) is applied to the electronic unit and the output reading is noted, using as simulator, and input voltage (V_i) is applied to the unit, of such a value that the resulting output reading equals that value previously noted.

The CMRR is calculated according as follows:

$$\text{CMRR} = 20 \log \frac{(V_c)}{(V_i)}$$

6.5 Test Procedures for Electrodes

6.5.1 *Resistance of Reference Electrodes*

Place the electrode to be tested and a platinum or silver wire in 3.5 mol l^{-1} KCl solution. Apply an alternating voltage of up to 5V with a frequency of 50 Hz or more and measure the alternative current through the circuit. The electrode resistance can be obtained by the following:

$$R = \frac{E_{\text{mean}}}{I_{\text{mean}}}$$

where

E_{mean} is the r.m.s. potential of the applied alternating voltage, and

I_{mean} is the r.m.s. of the measured alternating current.

NOTE — The use of commercially available conductivity meters or appropriate resistance meters can also be recommended, provided that they apply an alternating voltage to the external circuit.

6.5.2 *Flow Rate of Reference Electrode Electrolyte*

The test method may be selected by agreement between the manufacturer and the user. Two suitable methods are given (**6.5.2.1** and **6.5.2.2**).

The second method is particularly useful where several electrodes are to be tested simultaneously. Flow rates of less than 1 ml per day are measured by the first method. For higher rates, the second method may be used.

The first method requires the use of a high impedance voltmeter with a readability of 1 mV or less.

Differential pressure and temperature shall be constant for both methods and reported with results.

6.5.2.1 The electrode is filled with 3.5 mol l^{-1} KCl and placed in a beaker with known volume of distilled or double deionized water (approximately 20 ml) with chloride-sensitive electrode.

The electrode pair shall stand for 72 h or more, after which the potential is read in volts and the flow rate is determined as given below. Determine the concentration by reading from previously prepared calibration curves. The flow rate Q, in litres per hour, is then calculated from:

$$Q = \frac{cV}{c'}$$

where

c = final chloride concentration, in mol l^{-1}
V = volume of water in beaker, in litres
c' = chloride concentration in the reference electrode, in mole l^{-1}
t = test time, in hours.

6.5.2.2 The electrode is filled with KCl solution to rated level and the liquid junction is immersed in water for 72 h or more. Then the electrode is refilled to rated level again with KCl and the flow rate, Q is calculated from:

$$Q = \frac{V}{t}$$

where

V = volume of KCl solution for refill, in litres
t = test time, in hours

6.5.3 *Resistance of Glass Electrode*

The electrical resistance of a glass electrode is a function of glass composition membrane configuration, heat treatment during fabrication and temperature during measurement. dc resistance of glass electrodes is usually within the range of 10 M to 1 000 M at 25°C.

Place the electrode in any reference buffer solution which will give a potential reading against a low resistance (less than 100 k) reference electrode of at least 100 mV but preferably less than 500 mV.

Heat (or cool) the buffer solution to 25 ± 1°C.

Wait for a stable reading of e.m.f. and record it (E_1).

Shunt the input of the electronic unit with a known standard, screened, resistor R (for example, R = 100 m) and record the new stable e.m.f. reading (E_2).

Calculate and report the 25°C electrode resistance R_e from :

$$R_e\,(25°C) = R\,\frac{(E_1 - E_2)}{E_2}$$

NOTE — The high resistance resistor should be handled with care to avoid contamination which could result in an erroneous measurement. It should be stored in a clean container and handled only with gloved hands or tweezers.

6.5.4 *Sodium Error*

Alkali ions, and in particular the sodium ion, are the most important substances causing interference errors in glass electrodes. The sodium error depends on the glass composition of the electrode and on the concentration of the sodium ions in the sample, the *p*H value and the temperature of the sample.

ANNEX A

(*Clause* 3.2)

VALUES OF THE SLOPE FACTOR $K = 2.3026\ RT/F$

t (°C)	k (mV)	t (°C)	k (mV)	t (°C)	k (mV)	t (°C)	k (mV)
0	54.199	25	59.159	50	64.120	75	69.081
5	55.191	30	60.152	55	65.112	80	70.073
10	56.183	35	61.144	60	66.104	85	71.065
15	57.175	40	62.136	65	67.096	90	72.057
20	58.167	45	63.128	70	68.088	95	73.049

$R = 8.31441\ JK^{-1}\ mol^{-1}$

$F = 96.4856 \times 10^3\ C\ mol^{-1}$

T = thermodynamic temperature in kelvins

ANNEX B

(*Clauses* 6.1.4., 6.3.7.2, 6.3.8.2. and 6.3.9.2)

REFERENCE BUFFER SOLUTIONS : *p*H AS A FUNCTION OF TEMPERATURE

B.1 When reference materials are obtained from national metrology agencies, the certified values provided with each material should be used. Buffers *A* and *I* are useful at the low and high ends of the *p*H scale, respectively. However, because of liquid junction potential erroes, measurements made using these solutions, *A* and *I* should therefore not be chosen when measurements are to be made in the *p*H range of 3.5 to 10.

t (°C)	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
0	–	–	3.863	4.003	6.984	7.534	9.464	10.317	13.423
5	1.668	–	3.840	3.999	6.951	7.500	9.395	10.245	13.207
10	1.670	–	3.820	3.998	6.923	7.472	9.332	10.179	13.003
15	1.672	–	3.802	3.999	6.900	7.448	9.276	10.118	12.810
20	1.675	–	3.788	4.002	6.881	7.429	9.225	10.062	12.627
25	1.679	3.557	3.776	4.008	6.865	7.413	9.180	10.012	12.454
30	1.683	3.552	3.766	4.015	6.853	7.400	9.139	9.966	12.289
35	1.688	3.549	3.759	4.024	6.844	7.389	9.102	9.925	12.133
38	1.691	3.548	3.755	4.030	6.840	7.384	9.081	9.903	12.043
40	1.694	3.547	3.753	4.035	6.838	7.380	9.068	9.889	11.984
45	1.700	3.547	3.750	4.047	6.834	7.373	9.038	9.856	11.841
50	1.707	3.549	3.749	4.060	6.833	7.367	9.011	9.828	11.705
55	1.715	3.554	–	4.075	6.834	–	8.985	–	11.574
60	1.723	3.560	–	4.091	6.836	–	8.962	–	11.449
70	1.743	3.580	–	4.126	6.845	–	8.921	–	–
80	1.766	3.609	–	4.164	6.859	–	8.885	–	–
90	1.792	3.650	–	4.205	6.877	–	8.850	–	–
95	1.806	3.674	–	4.227	6.886	–	8.833	–	–

Compositions

A. 12.61 g potassium tetraoxalate, $KH_3(C_2O_4)_2 \, 2H_2O$, made up to 1 000 ml in water at 25° C.

B. Potassium hydrogen tartrate, $KHC_4H_4O_6$, saturated at 25° C.

C. 11.41 g potassium dihydrogen citrate, $KH_2C_6H_5O_7$, made up to 1 000 ml in water at 25°C.

D. 10.12 g potassium hydrogen phthalate, $KHC_8H_4O_4$, made up to 1 000 ml in water at 25°C.

E. 3.387 g potassium dihydrogen phosphate, KH_2PO_4 plus 3.533 g disodium hydrogen phosphate Na_2HPO_4, made up to 1 000 ml in water at 25°C.

F. 1.179 g KH_2pO_4 plus 4.303 g Na_2HPO_4, made up to 1 000 ml in water at 25°C.

G. 3.80 g sodium tetraborate decahydrate, $Na_2B_4O_7 . 10H_2O$, made up to 1 000 ml in water at 25°C.

H. 2.092 g sodium hydrogen carbonate, $NaHCO_3$ plus 2.640 g sodium carbonate, Na_2CO_3, made up to 1 000 ml in water at 25°C.

I. Calcium hydroxide, $Ca(OH)_2$ saturated at 25°C.

All reagents shall be of analytical grade and the conductivity of the water shall be equal to or less than 2µS cm^{-1}.

ANNEX C

(*Clause* 6.1.4)

TEST SOLUTIONS

C-1 Reference buffer solutions, as examplified in Annex B, being dilute solutions, have a limited buffering capacity. For practical applications, it is sometimes necessary to use buffers of higher capacity, even though their *p*H values are less certain (±.02). Examples of such technical buffer solutions follow. For accurate measurements, it is recommended that these solutions be calibrated against reference buffer solutions, before use.

t (°C)	*A*	*B*	*C*	*D*	*E*	*F*
0	1.08	-	4.67	6.89	9.48	-
10	1.09	3.10	4.66	6.84	9.37	13.37
20	1.09	3.07	4.65	6.80	9.27	12.96
25	1.09	3.06	4.65	6.79	9.23	12.75
30	1.10	3.05	4.65	6.78	9.18	12.61
40	1.10	3.04	4.66	6.76	9.09	12.29
50	1.11	3.04	4.68	6.76	9.00	11.98
60	1.11	3.04	4.70	6.76	8.92	11.69
70	1.11	3.04	4.72	6.76	8.88	11.43
80	1.12	3.05	4.75	6.78	8.85	11.19
90	1.13	3.07	4.79	6.80	8.82	10.99
β at 25°C	0.26	0.11	0.10	0.09	0.07	0.33

NOTE — The buffer value represents the change in *p*H [*d* (*p*H)] caused by the addition of an increment (d*N* moles) of an acid or a base. When the addition is made to a volume (V_o) of the initial solution, β is given by·

$$\beta = \frac{1}{V_o} \cdot \frac{dN}{d\,(pH)}$$

Compositions

A. 0.1 mol 1^{-1} HCl.

B. 20 g aminoacetic acid (glucine), NH_2CH_2COOH, 10 g NaCl and 50 ml 1 mol. 1^{-1} HCl made up to 1 000 ml in water at 25°C.

C. 100 ml 1 mol. 1^{-1} sodium hydroxide and 200 ml 1 mol. 1^{-1} acetic acid, made up to 1000 ml in water at 25°C.

D. 55.4 g disodium hydrogen phosphate, $Na_2HPO_4 . 12\,H_2O$, and 4.79 g citric acid, $HOC-(CH_2COOH)_2\,COOH$, made up to 1 000 ml in water at 25°C.

E. 1 000 ml 0.2 mol 1^{-1} boric acid, H_3BO_3 and 550 ml 0.2 mol 1^{-1} sodium hydroxide.

F. 0.1 mol 1^{-1} sodium hydroxide.

All reagent shall be of analytical grade and the conductivity of the water shall be equal to or less than 2μS cm.

ANNEX D

(*Clause* 6.3.5)

ALTERNATIVE PROCEDURES FOR MEASURING DELAY TIME (T_{10}) RISE (FALL) TIME (T_r, T_f) AND 90 PERCENT TIME (T_{90})

D-1 PROCEDURE A

A recorder is connected to the output terminals of the analyser. The sensor unit is place in a flow-through cell (as similar as possible to that cell used in the application) and equipped with a two-way stopcock to supply alternately reference buffer solutions with low and high *p*H values (diluted buffer solutions to reduce density effects). A reference buffer solution representing the minimum rated *p*H value is supplied until a constant reading on the recorder is obtained. Then the two-way stopcock is switched to supply a reference buffer solution representing the maximum rated *p*H value and a mark is made on the recorder chart. The maximum *p*H buffer solution is supplied until a constant reading is obtained. Then the stopcock is switched back to the minimum *p*H buffer solution and a second mark is made on the recorder

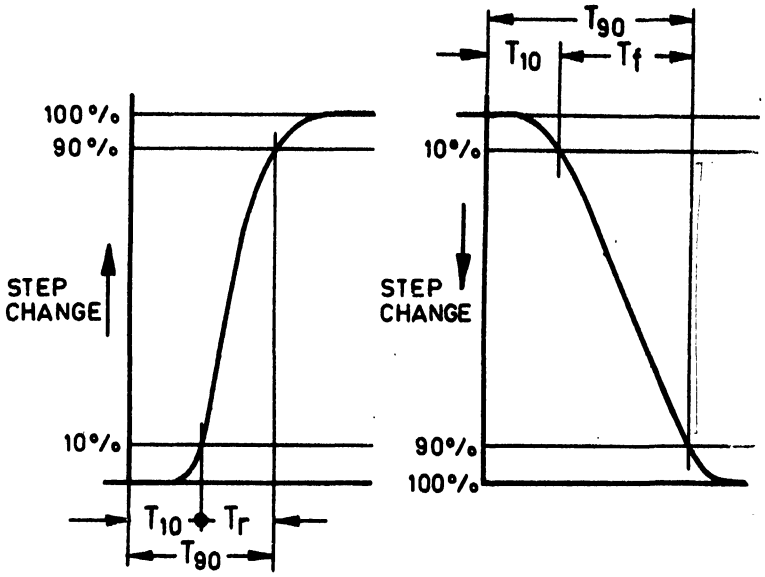

FIG. 1 RELATION BETWEEN T_{10}, T_r, T_f AND T_{90}

chart. Again, the minimum *p*H buffer solution is supplied until a constant reading is obtained.

The flow rate of the solution may be adjusted to the maximum specified by the manufacturer as the normal flow rate for the equipment. The temperature of the solutions and sensor unit shall be constant within ± 0.5°C and shall be reported with other results.

The values for delay time (T_{10}) and 90 percent time (T_{90}), for both increasing and decreasing step changes, rise time (T_r) and falt time (T_f), are determined through knowledge of the chart speed. The larger of the two delay times, the larger of rise or fall time and the larger of the two 90 percent times are reported.

D-2 PROCEDURE B

Similar to the above except that the sensor unit is immersed alternately in two different beakers, one containing a stirred buffer solution representing the minimum rated *p*H value and the other containing a stirred buffer solution representing the maximum rated *p*H value. When transferring the sensor unit from one beaker to the other, the sensor unit is shaken off but not wiped and rinsed. The sensor unit is left in the beakers until constant readings are obtained.

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